Name ____ AP Chemistry

The Determination of K_{eq} for $FeSCN^{2+}$

Introduction

There are many reactions that take place in solution that are equilibrium reactions; that is, they do not go to completion, both the forward and reverse reaction are occurring, and both reactants and products are always present in a fixed ratio of concentration. These ideas can be expressed mathematically in the form of the equilibrium constant. Consider the following general equation for a reversible chemical reaction:

$$aA + bB \leftrightarrow cC + dD$$

The equilibrium constant (K_{eq}) for this general reaction is given by the equation below, where the square brackets refer to the molar concentrations of the reactants and products at equilibrium:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The equilibrium constant gets its name from the fact that for any reversible chemical reaction, the value of K_{eq} is a constant at a particular temperature. The concentrations of reactants and products at equilibrium vary, depending on the initial amounts of materials present. The special ratio of reactants and products described by K_{eq} is always the same as long as the system has reached equilibrium and the temperature does not change. The value of K_{eq} can be calculated if the concentrations of reactants and products at equilibrium are known.

The reversible chemical reaction of iron (III) ions (Fe^{3+}) with thiocynate ions (SCN^-) provides a convenient example for determining the equilibrium constant of a reaction. As shown by the balanced chemical equation, Fe^{3+} and SCN^- ions combine to form a special type of combined or “complex” ion having the formula $FeSCN^{2+}$:

$$Fe^{3+}\text{ (aq)} + SCN^-\text{ (aq)} \leftrightarrow FeSCN^{2+}\text{ (aq)}$$

Pale yellow + Colorless ↔ Blood-red

The value of K_{eq} can be determined experimentally by mixing known concentrations of Fe^{3+} and SCN^- ions and measuring the concentration of $FeSCN^{2+}$ ions at equilibrium. The reactant ions are pale yellow and colorless, respectively, while the product ions are blood-red. The concentration of $FeSCN^{2+}$ complex ions at equilibrium is proportional to the intensity of the red color.

Compounds that are colored absorb a part of the visible spectrum of light. If a compound absorbs green light, it will appear red in color, the complementary color to green. A spectrophotometer is an instrument that measures the amount of light of a given wavelength or color that is absorbed by a solution. A colorimeter is a smaller device that uses a color filter in place of a prism or diffraction grating, as in a spectrophotometer. Both a colorimeter and spectrophotometer can determine the concentration of a colored solution using Beer's law:

$$A = \varepsilon b C$$

This mathematical relationship relates absorption of light (A) to the absorptivity of the sample (ε), cell path (b), and the molar concentration (C). When a sample is analyzed, the absorptivity of the sample is constant and the width of the cell path (the test tube or cuvette) does not change; therefore, the absorption read by a spectrophotometer or colorimeter is directly proportional to the concentration of the sample. A graph of absorption versus concentration will be a straight line.

In this experiment, the equilibrium constant for the reaction of iron (III) ions with thiocyanate ions will be calculated. First several reference solutions will be measured using the colorimeter to get the absorbance of each solution. From the known concentrations and the absorbances, a calibration curve will be created. Finally, solutions of unknown concentrations will be measured. Using the measured absorbance, the concentrations can be determined with the assistance of the calibration curve. Then the equilibrium constant can be calculated.

Prelab Questions

1) The reaction for the formation of the diamminesilver ion is as follows:

$$Ag^+ (aq) + 2\ NH_3 (aq) \leftrightarrow Ag(NH_3)_2^+ (aq)$$

   (a) Write the law of mass action for this reaction.
   (b) Using the data determined from an experiment below, calculate:
      (i) the equilibrium concentration of Ag^+
      (ii) the equilibrium concentration of NH_3
      (iii) the equilibrium constant

Total moles of Ag^+ present	3.6×10^{-3} moles
Total moles of NH_3 present	6.9×10^{-3} moles
Total volume	100 mL
Measured $[Ag(NH_3)_2^+]$ at equilibrium	3.4×10^{-2} M

2) Write the law of mass action for reaction with iron (III) and thiocyanate ions.

3) In this reaction, there is a large excess of Fe^{3+} ions being added so all of the SCN^- ions will be converted to $FeSCN^{2+}$ molecules. Therefore, the final concentration of $FeSCN^{2+}$ can be assumed to be equal to the initial concentration of SCN^- ions. Using the initial concentration and the initial volume of KSCN given below, calculate the final concentration of KSCN for each reference solution. Enter these values in Data Table 1 as $[FeSCN^{2+}]$. (Hint: remember the dilution formula ($M_1V_1 = M_2V_2$) and that V_2 in each reference solution is 10 mL).

Standard	**Volume of 0.00020 M KSCN Solution**
Reference solution #1	2.0 mL
Reference solution #2	3.0 mL
Reference solution #3	4.0 mL
Reference solution #4	5.0 mL
Reference solution #5	6.0 mL

Procedure

1) Obtain 4 small beakers or containers. Label them as the following: 0.200 M $Fe(NO_3)_3$, 0.0020 M $Fe(NO_3)_3$, 0.0020 M KSCN, and 0.00020 M KSCN.
2) Add the following amounts of each in the properly labeled beaker or container:
   - 30 mL of <u>0.200 M</u> $Fe(NO_3)_3$
   - 25 mL of <u>0.0020 M</u> $Fe(NO_3)_3$
   - 15 mL of <u>0.0020 M</u> KSCN
   - 20 mL of <u>0.00020 M</u> KSCN
3) Obtain 5 test tubes and 2 small (10 or 25 mL) graduated cylinders. Label the test tubes 1-5.
4) Label one graduated cylinder as Fe and another as KSCN.
5) Measure out 10 mL of water and fill each test tube with 10 mL of water. Mark the top of the water level on the glass with a permanent marker. This will serve as a volume of 10 mL.
6) Using the chart below, add the correct volume for each solution to the appropriate test tubes. Use one graduated cylinder for the iron solution and the other for the thiocyanate solution.
   Note: You are using **0.200 M $Fe(NO_3)_3$ and 0.00020 M KSCN** solutions. Pay attention to the concentrations!

Standard	**Volume of 0.200 M $Fe(NO_3)_3$ Solution**	**Volume of 0.00020 M KSCN Solution**
Reference solution #1	8.0 mL	2.0 mL
Reference solution #2	7.0 mL	3.0 mL
Reference solution #3	6.0 mL	4.0 mL
Reference solution #4	5.0 mL	5.0 mL
Reference solution #5	4.0 mL	6.0 mL

7) Stir each solution with a stirring rod. Make sure to rinse with DI water between solutions. Allow the solutions to sit for 10 minutes to reach equilibrium.
8) Follow the instructions provided by the instructor in using the colorimeter. Measure the absorbance of each solution and record that absorption in Data Table 1.
9) Take the temperature of one solution and record it in Data Table 1.
10) Place all solutions in the waste container and rinse all of the test tubes and graduated cylinders.
11) Using the chart below, add the correct volume for each solution to the appropriate test tubes. Use one graduated cylinder for the iron solution and the other for the thiocyanate solution.
    Note: You are using **0.0020 M $Fe(NO_3)_3$ and 0.0020 M KSCN** solutions. Pay attention to the concentrations!

Sample	**Volume of 0.020 M $Fe(NO_3)_3$ Solution**	**Volume of 0.0020 M KSCN Solution**
Test solution #1	5.0 mL	1.0 mL
Test solution #2	5.0 mL	2.0 mL
Test solution #3	5.0 mL	3.0 mL
Test solution #4	5.0 mL	4.0 mL
Test solution #5	5.0 mL	5.0 mL

12) Add DI water to the marked line on each test tube. Stir each solution with a stirring rod. Make sure to rinse it with DI water between solutions.
13) Allow the solutions to sit for 10 minutes to reach equilibrium.
14) Follow the instructions provided by the instructor in using the colorimeter. Measure the absorbance of each solution and record that absorption in Data Table 1.
15) Take the temperature of one solution and record it in Data Table 1.
16) Place all solutions in the waste container and rinse all of the test tubes and graduated cylinders.

Results

Data Table #1: Reference Solutions

Temperature		
Sample	**[$FeSCN^{2+}$]**	**Absorbance**
Reference solution #1		
Reference solution #2		
Reference solution #3		
Reference solution #4		
Reference solution #5		

Data Table #2: Test Solutions

Temperature			
Sample	**[Fe^{3+}]**	**[SCN^-]**	**Absorbance**
Test solution #1			
Test solution #2			
Test solution #3			
Test solution #4			
Test solution #5			

Data Table #3: Calculations

Sample	**[$FeSCN^{2+}$]$_{eq}$**	**[Fe^{3+}]$_{eq}$**	**[SCN^-]$_{eq}$**	**K_{eq}**
Test solution #1				
Test solution #2				
Test solution #3				
Test solution #4				
Test solution #5				
			Average	

Calculations

1) In a graphing program, plot the molar concentration of $FeSCN^{2+}$ ions (x-axis) versus the absorbance (y-axis) from Data Table 1. Plot the best-fit line. Make sure to include the equation of the line.
2) Using the equation of the line, calculate the unknown concentration of $FeSCN^{2+}$ for each test solution (Hint: Y is the absorbance while x is the molar concentration). Write each concentration in Data Table 3 under [$FeSCN^{2+}$].
3) Use the dilution formula ($M_1V_1 = M_2V_2$) to calculate the final concentrations of Fe^{3+} and SCN^- solutions before the reaction occurs. Enter these values in Data Table #2 as either [Fe^{3+}] or [SCN^-].
   Note: Refer to the table in step #11 of the procedure for the different volumes. Remember that V_2 is 10 mL.
4) Calculate the equilibrium concentration of Fe^{3+} in each test solution using the following formula: $[Fe^{3+}]_{eq} = [Fe^{3+}]_{initial} – [FeSCN^{2+}]_{eq}$. Write each concentration in Data Table 3 under $[Fe^{3+}]_{eq}$.
5) Calculate the equilibrium concentration of SCN^- in each test solution using the following formula: $[SCN^-]_{eq} = [SCN^-]_{initial} – [FeSCN^{2+}]_{eq}$. Write each concentration in Data Table 3 under $[SCN^-]_{eq}$.

6) Using your answer from Prelab #2, calculate K_{eq} for each test solution. Average the equilibrium constant values.

Postlab Questions

1) Was the value constant for all your experiments? Should it be constant?
2) What does the magnitude of the equilibrium constant tell you about the extent of reaction (i.e. is reactants or products favored)?
3) Would the measured value of K_{eq} change if this experiment had been conducted at 50°C instead of ambient temperature? Explain.
4) The equilibrium concentration of $FeSCN^{2+}$ ions in each reference solution is essentially equal to the concentration of SCN^- ions in solution before any reaction occurs. Use LeChâtelier's principle to explain why this statement is true.